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Schwinger multichannel method: A study of a Feshbach resonance in e-H_2 collisions

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We present results of the application of the Schwinger multichannel method to study the role of Feshbach resonances on the elastic and electronic excitation cross sections in e-H_2 collisions. Using a $^2\Sigma_g^+$ resonance associated with the $a\,^3\Sigma_g^+$ and $E\,^1\Sigma_g^+$ states of H_2 as an example, we quantitatively illustrate the dramatic influence of open channels on the decay of such Feshbach resonances in electron-molecule collisions.

Feshbach and core-excited shape resonances play an important role in the cross sections for electronic excitation of molecules in the important near-threshold region.[1] Features associated with such resonances have been widely studied experimentally in diatomic and other molecules.[1-3] Theoretical studies of these Feshbach resonances in molecules have focused on the determination of their positions in the electron impact spectra using bound-state techniques based on the stabilization,[4] projection operator,[5] and quasivariational[6] methods. Such studies have not provided scattering cross sections. Several approaches—the R matrix,[7-10] linear algebraic,[11,12] the Schwinger multichannel (SMC),[13-15] and Kohn[16] methods—which have been used to determine cross sections for electronic excitation of molecules, can also be used, in principle, to study the influence of Feshbach resonances on these excitation cross sections. Cross sections for e-H_2^+ collisions, including the effects of Feshbach resonances below the first excitation threshold, have been studied using the R matrix and linear algebraic methods.[7,8,11]

In this Rapid Communication we present results of the first application of the Schwinger multichannel method to study the role of a Feshbach resonance on the cross sections for electronic excitation of H_2. The specific case we discuss is that of a $^2\Sigma_g^+$ resonance associated with the $a\,^3\Sigma_g^+$ state of H_2 and its influence on the elastic and the $X\,^1\Sigma_g^+ \rightarrow b\,^3\Sigma_u^+$ excitation cross sections. *Our primary objective is not to carry out a highly quantitative study of a specific Feshbach resonance in this system, but to realistically identify some salient dynamical features that can arise in the cross sections from these resonances.* For example, with our specific choice of target and channel expansion of the total scattering wave function, the $^2\Sigma_g^+$ resonance state lies about 60 meV below its $a\,^3\Sigma_g^+$ parent. Although we certainly expect its position relative to this parent to change with improvements in both the target and $(N+1)$-scattering wave function, what is important here is that *it is a Feshbach resonance at this level of approximation* and provides a useful example for studying features such as (i) the dynamics of coupling of molecular Feshbach resonances to elastic and electronically inelastic channels, (ii) the presence of correlation terms, e.g., $1\sigma_g 2\sigma_g^2$, in the scattering wave function and their influence on the proper choice of open and closed channels, and (iii) how to approach these problems with the SMC method.

The SMC formulation has been discussed extensively elsewhere.[13,17] It is an L^2 approach to electron-molecule collisions in which the open- and closed-channel spaces are incorporated via a projected Lippmann-Schwinger and Schrödinger equation, respectively. With an expansion of the scattering wave function in Cartesian Gaussians all spatial integrations arising in our procedure for the evaluation of matrix elements in the associated variational expression *can be done analytically for an arbitrary molecular target.* In contrast to earlier applications of this method,[14,15] in the present studies integrations over linear momentum variables required in the second-Born-like term, i.e., $\langle\tilde{\Psi}|VG_p^{(+)}V|\tilde{\Psi}\rangle$, are obtained via a three-dimensional quadrature.[18] With this procedure we find that relatively small basis sets can provide reliable scattering cross sections. This property is particularly advantageous in the present application where narrow features in

the cross sections are of interest and require calculations on a fine energy grid, e.g., at 0.01-eV intervals.

In these studies our channel expansion of the scattering wave function includes the $X\,^1\Sigma_g^+(1\sigma_g^2)$, $b\,^3\Sigma_u^+(1\sigma_g 1\sigma_u)$, $a\,^3\Sigma_g^+(1\sigma_g 2\sigma_g)$, $E\,^1\Sigma_g^+(1\sigma_g 2\sigma_g)$ (the inner loop of the E, $F\,^1\Sigma_g^+$ state), and $B\,^1\Sigma_u^+(1\sigma_g 1\sigma_u)$ states. For the ground state we used a self-consistent-field (SCF) wave function obtained with a $4s$ (13.3615, 2.0133, 0.453757, 0.123317) and $2s$ (0.25, 0.01) Cartesian basis on each hydrogen and on the molecular center, respectively. The exponents of these functions are shown in parentheses. This basis gives a ground SCF energy of -1.1267 a.u. at the equilibrium internuclear distance of 1.4 a.u., where all calculations were carried out, and static-exchange elastic cross sections in good agreement with known accurate values. For convenience, we also only report cross sections for the dynamically important $^2\Sigma_g$ symmetry. Contributions from other symmetries, e.g., $^2\Sigma_u$, $^2\Pi_u$, $^2\Pi_g$, etc., would only affect the background. For the $b\,^3\Sigma_u^+$ and $a\,^3\Sigma_g^+$ states we used a frozen-core approximation and obtained the $1\sigma_u$ and $2\sigma_g$ orbitals by diagonalizing the V_{N-1} potential in the same basis. The resulting vertical excitation energies for the $b\,^3\Sigma_u^+$ and $a\,^3\Sigma_g^+$ states were 10.068 and 12.521 eV, respectively, compared to the "experimental" vertical excitation energies of 10.35 and 12.28 eV from the $v=0$ level. For the corresponding singlet states, the $B\,^1\Sigma_u^+$ and $E\,^1\Sigma_g^+$, we used the spatial orbitals of the triplet calculation but with the appropriate spin coupling. This choice greatly simplifies the solution of the scattering equations and is required by the present computer codes. More importantly, for the present studies this restriction does not introduce any severe limitation in our "model." The calculated excitation energies for the $B\,^1\Sigma_u^+$ and $E\,^1\Sigma_g^+$ (E,F) states are 15.429 and 13.661 eV, respectively, compared with the values of 12.5 and 12.8 eV from the $v=0$ level of the ground state given by the accurate potential-energy curves of Sharp.[19] Since our interest is in the role of these singlet states as closed channels, the fact that our calculated excitation energies are larger than the experimental values is not crucial.

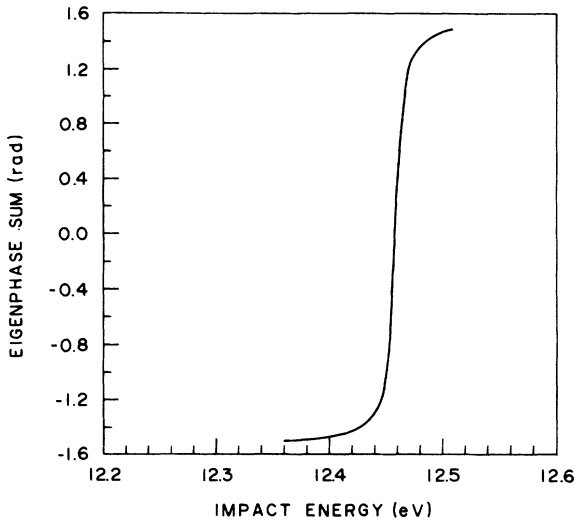

FIG. 2. $^2\Sigma_g^+$ eigenphase sum for elastic e-H_2 scattering with the $a\,^3\Sigma_g^+$ and $E\,^1\Sigma_g$ states as closed channels.

We will first highlight a few significant dynamical features emerging from these studies. First, the solid curve in Fig. 1 shows the very pronounced dip in the elastic cross sections produced by a Feshbach resonance primarily associated with the $a\,^3\Sigma_g^+$ state. The resonant character of the cross section can also be seen in the eigenphase sum shown in Fig. 2. The long-dashed curve in Fig. 1 shows the dramatic change in these cross sections brought about when the energetically open $b\,^3\Sigma_u^+$ channel is included in the calculation. The long-dashed curve of Fig. 3 shows that the Feshbach resonance now preferentially decays into the inelastic $b\,^3\Sigma_u^+$ channel over the elas-

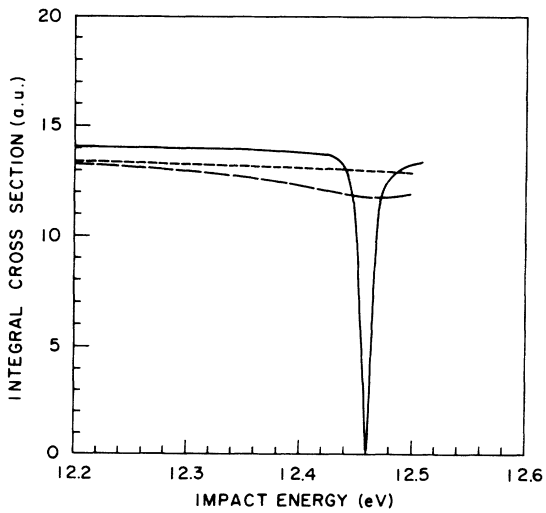

FIG. 1. $^2\Sigma_g^+$ integrated cross sections for e-H_2 elastic cross section: ——, with the $a\,^3\Sigma_g^+$ and $E\,^1\Sigma_g$ states included as closed channels; – – –, with the $a\,^3\Sigma_g^+$, $E\,^1\Sigma_g$, and $B\,^1\Sigma_u$ states as closed channels, and the $b\,^3\Sigma_u$ state open; ---, $E\,^1\Sigma_g$ and $B\,^1\Sigma_u^+$ states as closed channels and the $b\,^3\Sigma_u^+$ open.

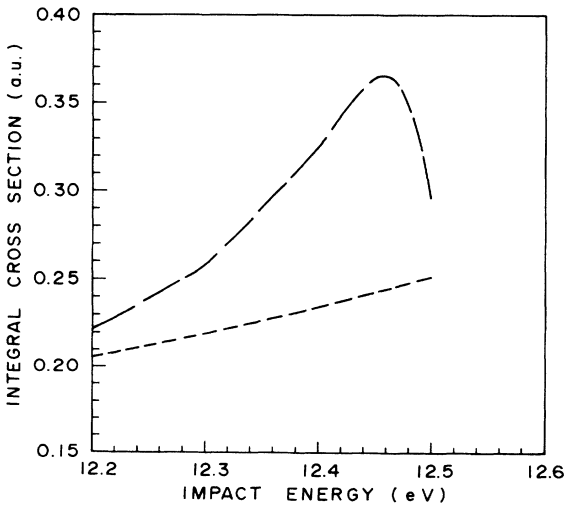

FIG. 3. $^2\Sigma_g^+$ integrated cross sections for excitation of the $X\,^1\Sigma_g^+ \rightarrow b\,^3\Sigma_u^+$ transition: – – –, with the $a\,^3\Sigma_g^+$, $E\,^1\Sigma_g$, and $B\,^1\Sigma_u$ states as closed channels and the $b\,^3\Sigma_u$ state open; ---, $E\,^1\Sigma_g$ and $B\,^1\Sigma_u^+$ states as closed channels and the $b\,^3\Sigma_u^+$ open.

tic channel. The short-dashed curves in Figs. 1 and 3 show that this resonance behavior is no longer seen in the elastic and inelastic cross sections at this energy when the dominant $a\,^3\Sigma_g^+$ parent state is removed from the calculation. In the next few paragraphs we will give further details of the multichannel dynamics underlying these important features in electron-molecule scattering cross sections arising from Feshbach resonances. To our knowledge these results represent the first attempt to quantitatively incorporate the role of such resonances in electronic excitation of molecules by low-energy electrons.

To begin we consider a calculation with three target states, the $X\,^1\Sigma_g^+(1\sigma_g^2)$, the $a\,^3\Sigma_g^+(1\sigma_g 2\sigma_g)$, and the $E\,^1\Sigma_g^+(1\sigma_g 2\sigma_g)$ states. In the SMC method the $(N+1)$-scattering wave function ($^2\Sigma_g^+$) is made up of three types of configurations, the elastic $A\{[X\,^1\Sigma_g^+(1\sigma_g^2)]n\sigma_g\}$, the triplet coupled $A\{[a\,^3\Sigma_g^+(1\sigma_g 2\sigma_g)]n\sigma_g\}$, and the singlet coupled $A\{[E\,^1\Sigma_g^+(1\sigma_g 2\sigma_g)]n\sigma_g\}$ terms. Here $n\sigma_g$ runs over all possible σ_g orbitals, including the $2\sigma_g$ in which case the resulting triplet- and singlet-coupled configurations $1\sigma_g 2\sigma_g^2$ are equivalent, and A is an antisymmetrizer. To obtain the approximate positions of possible resonances we next diagonalize the $(N+1)$ Hamiltonian in the space of these SMC configurations. We now focus on the root at 12.466 eV above the $X\,^1\Sigma_g^+$ state, 0.055 eV below the $a\,^3\Sigma_g^+$ state, and 1.195 eV below the $E\,^1\Sigma_g^+$ state. The dominant component of this root is the so-called correlation term $1\sigma_g 2\sigma_g^2$ (Ref. 12). It is thus not possible to assign the parentage of this Feshbach resonance to the $a\,^3\Sigma_g^+$ state alone since this correlation term can also be obtained by antisymmetrization of the product $A\{[E\,^1\Sigma_g^+(1\sigma_g 2\sigma_g)]2\sigma_g\}$. The solid curve in Fig. 1 shows the sharp dip in the elastic cross section at 12.460 eV, very close to this root of the $(N+1)$ Hamiltonian.

Figure 1 also shows the elastic cross sections (long-dashed curve) obtained when the $b\,^3\Sigma_u^+(1\sigma_g 1\sigma_u)$ and $B\,^1\Sigma_u^+(1\sigma_g 1\sigma_u)$ states are included in the calculation as open and closed channels, respectively. These channels introduce configurations of the type $A\{[b\,^3\Sigma_u^+(1\sigma_g 1\sigma_u)] \times n\sigma_u\}$ and $A\{[B\,^1\Sigma_u^+(1\sigma_g 1\sigma_u)]n\sigma_u\}$ into the scattering-wave-function expansion. The opening of this $b\,^3\Sigma_u^+$ channel is seen to completely change the collision dynamics in this region by moving flux between the elastic (long-dashed curve of Fig. 1) and the inelastic (long-dashed curve of Fig. 3) channel. Removal of all configurations associated with the $a\,^3\Sigma_g^+$ parent from the expansion of the wave function leads to the cross sections shown by the short-dashed curves of Figs. 1 and 3. Search of these elastic and inelastic cross sections at higher energies reveals that this resonant feature now moves closer to its singlet parent $[E\,^1\Sigma_g^+(1\sigma_g 2\sigma_g)]$. Although not shown in these figures, these resonances become significantly broader since they lie much further below their remaining parent.

These studies on e-H_2 collision clearly demonstrate that channels lying below a Feshbach resonance can strongly influence the decay of this resonance. Realistic calculations of these cross sections can hence, in general, require the inclusion of all such open channels. Details of the above studies including differential cross sections and other target states such as the $c\,^3\Pi_u$ and $C\,^1\Pi_u$ for H_2 as well as those of related studies for NO are under way.

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